

Encapsulation of Pesticides within a Starch Matrix

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At the Northern Regional Research Center, a research program is directed towards developing agriculturally based raw materials as renewable resources for chemicals to replace in part those derived from petroleum. Starch, a polysaccharide produced in great abundance in nature, is a prime candidate as a raw material because of its availability and relatively low cost and because it can be converted readily into a variety of useful monomeric and polymeric products by chemical and biochemical means. A low-cost derivative, starch xanthate, is useful in papermaking applications (1), for reinforcement of rubber (2), in making powdered rubber (3), and for removing heavy metals from polluted water (4). Because of the ease with which starch xanthate can be insolubilized from an aqueous solution by crosslinking under mild oxidation conditions or with metal cations, and because of the film-forming nature of certain crosslinked products, we explored the possibility of using this material as an encapsulating matrix for pesticides. We envisioned that release of a lipophilic pesticidal chemical from a hydrophilic but water-insoluble starch matrix would be slow and could be controlled to a considerable degree by simple modifications. Such a matrix would have an added advantage of being biodegradable and thus would leave no residue in the environment.

A preliminary report (5) described our first attempts to utilize oxidatively coupled starch xanthate (xanthide) as a slow-release matrix for pesticides and suggested that such a system was worthy of further research in attempts to optimize release characteristics. We now wish to report the results of our further studies and data from preliminary field tests with selected formulations.

The procedure based on starch xanthate consists of dispersing the active agent in an aqueous starch xanthate solution and subsequently crosslinking the starch xanthate either oxidatively, or with multivalent metal ions, or with difunctional reagents such as epichlorohydrin. Cereal flours, which contain about 10% protein along with starch, also can be xanthated and used as an encapsulating matrix. Upon crosslinking, which is effected within a few seconds under ambient conditions, the entire mass becomes gellike and, on continued mixing for an additional few seconds, becomes a particulate solid which can be dried to low moisture content with only minimal or no loss of the entrapped chemical. That only a single phase is produced on crosslinking with no supernatant is important in assuring essentially complete entrapment of both water-soluble and water-insoluble pesticidal chemicals.

Other polymers can be incorporated readily into the products as a means to modify release properties. Polymers like polystyrene, polyethylene, and poly(vinyl chloride) are just dissolved in a small amount of an appropriate solvent such as benzene or acetone then added to the xanthate solution. Poly(styrene-butadiene), commercially provided as a latex, is conveniently added in this form. Upon crosslinking the xanthate, the other polymers are entrapped along with the active agents.

Another modification easily made which can modify release properties provides products which are doubly encapsulated. This is achieved on addition of more starch xanthate, either alone or containing another polymer, after the initial crosslinking reaction has been effected and then adding additional crosslinking agent.

The starch xanthate used for encapsulation is prepared under ambient conditions by treating a water suspension of starch with carbon disulfide and an alkali metal hydroxide. Typically about 70% of the carbon disulfide is converted to xanthate within 30 minutes with little or no additional conversion occurring on prolonged standing. Although the theoretical number of xanthate groups possible for each anhydroglucose repeating unit of starch is 3 [degree of substitution (DS) of 3], we find that a DS of 0.1 to 0.35 is sufficient. Viscosity of xanthate solutions increases proportionally with DS and starch xanthate concentration. When whole unmodified starch (regular pearl starch) is used as the starting material, a starch xanthate concentration of near 15% is about the maximum that can be handled for the encapsulation process. Higher concentrations, usable in this process, of up to nearly 60% can be achieved, if the starting starch is reduced in molecular size by hydrolysis of some of the glucopyranosyl linkages with acids or enzymes.

Such modifications are conventional commercial procedures designed to provide degraded starch products for a variety of industrial uses.

Use of the more concentrated starch xanthate solutions has an obvious advantage in cost for drying the particulate encapsulated product. However, there are certain limitations on using the highly concentrated solutions. The amount of active agent that can be effectively encapsulated within the crosslinked starch xanthate matrix is inversely proportional to starch xanthate concentration. For example, when starch xanthate of 14% concentration is used, a final product is obtained which contains a maximum of 47% of a liquid thiocarbamate. When 50% xanthate is employed the maximum is reduced to 13%.

The values conceivably might vary with the nature of the chemical to be encapsulated. For the examples given, the active agent was butylate* (S-ethyl diisobutylthiocarbamate). At the highest level, where the particulate product consists of nearly 50% of the highly volatile liquid butylate, the particles have a wetted appearance and are not completely free flowing. At about 40% or less, they appear dry and give a free-flowing product.

Although various methods have been employed for crosslinking the xanthate with apparently similar results, we have worked mostly with the oxidative method and have used either nitrous acid or hydrogen peroxide as the selected oxidant. Both oxidants effectively crosslink the xanthate

to xanthide (starch-O- $\overset{\text{S}}{\underset{\text{S}}{\text{C}}}$ -S-S- $\overset{\text{S}}{\underset{\text{S}}{\text{C}}}$ -O-starch) at a pH of 4 to 5. Since the xanthate is made under alkaline conditions, the pH must be lowered to allow crosslinking. For pesticides, which are labile to alkali, the pH can be adjusted to near neutrality before addition of the active agent. For the nitrous acid system, sodium nitrite is added to the alkaline xanthate solution and becomes the active oxidant when the pH is lowered to 4-5. When peroxide is used, it is added to a neutralized xanthate and then pH is lowered further. Only slightly more than stoichiometric amounts of oxidant are required, and since the oxidation proceeds to completion rapidly, even active agents which are susceptible to oxidation are not likely to be oxidized during encapsulation. Although

* This paper reports the results of research only. Mention of a pesticide in this paper does not constitute a recommendation for use by the U.S. Department of Agriculture nor does it imply registration under FIFRA as amended. Also, mention of firm names does not constitute an endorsement by the U.S. Department of Agriculture over other firms not mentioned.

both oxidants appear to work equally well in crosslinking the xanthate, encapsulated products are quite different in appearance and in release properties of the active agent. Nitrous acid crosslinked products contain numerous microscopic openings in the matrix, due apparently to small amounts of nitrous oxide gas generated during the reaction. These openings result in a relatively rapid rate of release as will be described later. The peroxide-coupled products are without visible openings and provide much slower release of active agent.

Shelf life of the starch-encapsulated pesticides is good, and there is no appreciable loss on storage in closed containers during 1 year. When placed in open containers for several days, loss of volatile agent is negligible. However, when products are wetted or immersed in water, active agent is then released from the matrix. We devised a simple laboratory screening test for comparing release properties of thiocarbamate- containing products to assist in selection of formulations for subsequent bioassay. The test consists of placing several 1-gram portions of a product in watch glasses placed in a hood and applying to each 2-ml of water. The water slowly evaporates during a 24-hour period in the hood. Then water is again added and the wetted product again allowed to stand for 24 hours. This repeated wetting and drying is continued for the duration of the test with entire 1-gram samples being removed periodically and analyzed for total nitrogen content in those instances where the active agent contains nitrogen. Table I shows the release characteristics for four different formulations containing butylate.

Table I
Release Properties of Butylate Formulations

Xanthate base ^a	Loss of butylate, %		
	1 day	2 days	8 days
Acid-modified flour ^b	29	58	68
Acid-modified flour-starch mixture ^c	20	36	48
Starch	0	0	8
Starch + 20% latex ^c	0	0	37
None (control)	68	98	100

^a Xanthate DS was 0.35 and double encapsulation was used for each.

^b NaNO₂ used for oxidation.

^c H₂O₂ used for oxidation.

It would appear that either the protein component in the flour or the lower molecular weight of the starch component of the flour contributes to a faster release of butylate; however, this remains to be confirmed. Other preliminary tests indicate that DS of xanthate, e.g., crosslink density of the matrix, may play a significant role in controlling release of active agent, and studies to confirm this are underway.

Depending on the amount of shear placed on the particulate product before drying, a range of particle sizes can result. With simple hand mixing, a particle size of 14 mesh or larger is typically obtained. For small laboratory preparations, we shear the wet product in a Waring Blendor for a few seconds to produce smaller particle sizes.

We have not as yet attempted to provide products fine enough to pass 100 mesh. Grinding or milling the dried products can yield fine powders but considerable amounts of pesticide are lost, especially if they are highly volatile ones. Whereas shearing of the wet product results mostly in breaking up the agglomerates composed of several smaller particles, grinding or milling of dry products disrupts the matrix encapsulating the pesticide.

A product prepared from starch xanthate of DS 0.175 and crosslinked with H_2O_2 in the presence of EPTC (S-ethyl dipropylthiocarbamate) was dried and separated into four fractions by sieving. The four fractions were analyzed for active agent content and loss of agent after treatment with water for 2 days. Results are shown in Table II.

Table II
Properties of Starch Xanthide-EPTC Formulations
as Related to Particle Size

<u>Mesh size</u>	<u>% of Total</u>	<u>EPTC, %</u>	<u>Loss of EPTC after water treatment, % of total</u>
>60	5	14.0	14
30-60	10	21.7	17
14-30	70	21.7	5
<14	15	21.7	5

Except for the 5% fraction which passed 60 mesh, there was no difference in the amount of pesticide contained in the particles of various sizes. It does appear that smaller size particles release EPTC at a faster rate.

Some of the formulations we have prepared have been evaluated by others in various laboratory bioassay tests and, in one instance, in replicated field plots. Although the data obtained are encouraging and indicate considerable promise for the starch technology, it should be understood that the data are preliminary and that the formulations tested are by no means the optimum formulations that can be developed. That the release properties of various pesticides from the crosslinked starch or flour xanthate matrix can be considerably improved through minor modifications in the encapsulation process is strongly supported by our continuing research.

Feldmesser et al. (6) reported on laboratory evaluations of starch xanthide formulations of DBCP (1,2-dibromo-3-chloropropane), a nematicide, and diazinon [O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl)] phosphorothioate, an insecticide-nematicide for nematocidal activity. Two DBCP formulations containing 35.6% and 42.0% active agent and two diazinon ones containing 42.0 and 43.6% active were studied. To determine retention of active agent under various conditions, the products were aerated both wet and dry in open dishes for several days and then amount retained was determined by bioassays against nematodes in a standard *in vitro* test. During 10 days aeration of wet DBCP formulations, most of the active agent was lost and their subsequent effectiveness for killing nematodes was minimal. Retention of diazinon was considerably greater, perhaps due to its much lower vapor pressure than DBCP. During the 10-day aeration tests and an additional 34 days of aeration in the dry, the two diazinon formulations lost only about 20-33% of their active ingredient. The mortality of *Panagrellus redivivus*, a saprophagous nematode, after 48 hours exposure to 200 ppm diazinon in the form of the two starch xanthide formulations after various periods of aeration is shown in Table III.

Cooperative work is continuing between Feldmesser's and our Laboratories in attempts to develop formulations capable of effectively killing nematodes over an extended period.

Whereas many herbicides must be incorporated in the soil soon after application to the surface to prevent extensive losses due to volatilization or decomposition by sunlight, it is hoped that controlled release formulations may prolong the time before incorporation is needed, or ideally, to provide control without being incorporated. Four formulations containing butylate prepared by us were evaluated in the laboratory by Stauffer Chemical Company for the ability to delay time before incorporation. Butylate as an emulsifiable concentrate (EC) was applied as a control. Rates of active agent (ai) of 3 and 4 lb/A were applied. Formulations were placed on the surface of wet soil and incorporated immediately and after 24 hours. Results are shown in Tables IV and V.

Table III
Release Properties of Starch Xanthide-Diazinon Formulation

	Percent kill			
	42.0%		43.6%	
	<u>10 days</u>	<u>44 days</u>	<u>10 days</u>	<u>44 days</u>
<u>Starch-diazinon</u>				
Wet ^a	69.4	63.0	76.3	52.5
Dry	66.2	63.1	75.4	70.0
Unaerated ^b	74.6	76.0	78.1	74.3
<u>Technical diazinon</u>				
Wet ^a	81.0	0	82.8	0
Dry	76.6	0	77.4	0
Unaerated ^b	89.0	0	95.1	0

^a Second aeration period of 34 days following 10 day wet and dry aeration and 48 hours exposure was dry for all granules.

^b Granules not aerated for first 10 days. Aerated dry for 34 days.

Table IV
Percent Weed Control^a by Delayed Incorporation
of Butylate Formulations

<u>Formulation</u>	<u>Rate</u>	<u>Incorporation</u>	
		<u>0 Hours</u>	<u>24-Hour delay</u>
SX-butylate ^b	3 lb ai/A	80	75
SX-butylate ^c	3 lb ai/A	85	67
Butylate (EC)	3 lb ai/A	87	10

^a Average control of barley, foxtail, watergrass, wild oat, crabgrass, annual ryegrass, and shattercane.

^b Starch xanthate of DS 0.3; NaNO₂ was used for crosslinking; about 25% butylate.

^c Same as b except containing 35% butylate.

Table V
Percent Weed Control by Delayed Incorporation
of Butylate Formulations

<u>Formulation</u>	<u>Rate</u>	<u>Incorporation</u>	
		<u>0 Hours</u>	<u>24-Hour delay</u>
SX-butylate ^a	4 lb ai/A	77	68
SX-butylate ^b	4 lb ai/A	79	69
Butylate (EC)	4 lb ai/A	82	28

^a Starch xanthate of DS 0.3; NaNO₂ used for crosslinking; 25.5% butylate.

^b Same as a except larger particle size.

Although the results are preliminary, a benefit is seen for the encapsulated products in allowing a longer time on the soil surface before incorporation.

Schreiber (7), at Purdue University, recently reported results of greenhouse and field tests of two starch xanthide-EPTC products. The formulations were made from starch xanthates of DS 0.35, and sodium nitrite was used for crosslinking. One formulation contained 14% EPTC and the other was a double-encapsulated product containing 20% latex polymer and 22% EPTC. In the greenhouse, the double-encapsulated product was compared with EPTC applied as the emulsifiable concentrate. The materials were applied to soils at a rate of 3 lb/A and were incorporated into soils seeded with robust purple foxtail.

At 31 days after seeding, the plants were removed and weighed and the pots reseeded. This procedure was repeated at 52 and 87 days and the final harvest was at 120 days. Results are shown in Table VI.

Table VI
Weed Control by Starch Xanthide-EPTC Formulation

<u>Treatment</u>	<u>Yield, g/pot</u>			
	<u>31 Days</u>	<u>52 Days</u>	<u>87 Days</u>	<u>120 Days</u>
Untreated	1.6	2.0	2.8	2.2
EPTC (EC)	0	0.1	2.7	2.8
Starch xanthide-EPTC	0	0.01	0.4	3.9

At 31 and 52 days, both the EC and the starch xanthide formulations gave excellent control of foxtail. However, between 52 and 87 days, the EC completely lost its effectiveness while the starch product still gave good control. Between 87 and 120 days, the starch product lost its effectiveness. The greater weight of plant material in both treated pots over the control is due to the greater fertility level remaining in the soil of these pots.

In the field, the EC, single-encapsulated and double-encapsulated products were applied at active ingredient levels of 3 and 6 lb ai/A, incorporated, and overseeded with yellow, giant, and giant green foxtail. Natural populations of pigweed, lambsquarter, smartweed, jimson, and velvetleaf were the dominant broadleaf weeds. Forty-seven days after application, weed stand counts and weed weights by species were made on each plot. Results are shown in Table VII.

Table VII
Weed Control by Single and Double
Encapsulated EPTC Formulations

<u>Treatment^a</u>	<u>Total weed</u>	
	<u>Count</u>	<u>Weight, g</u>
Untreated	95.3	924.8
EC-EPTC	48.0	247.8
Starch-EPTC (single)	33.7	186.0
Starch-EPTC (double)	33.0	31.0

^a Applied at a rate of EPTC of
3 lb/A.

When applied at the 6 lb ai/A level, excellent control of all vegetation was obtained 105 days after treatment with the double-encapsulated formulations.

Cooperative work between Schreiber's Laboratory and ours is continuing with plans made for extensive field testing during 1977.

Literature Cited

1. Hamerstrand, G. E., Carr, M. E., Hofreiter, B. T., and Russell, C. R. Staerke (1976) 28(7):240-243.
2. Buchanan, R. A., Seckinger, H. L., Kwolek, W. F., Doane, W. M., and Russell, C. R. J. Elast. Plast. (1976) 8(1):82-95.
3. Abbott, T. P., James, C., Doane, W. M., and Russell, C. R. J. Elast. Plast. (1975) 7(2):114-132.
4. Wing, R. E., Doane, W. M., and Russell, C. R. J. Appl. Polym. Sci. (1975) 19(3):847-854.
5. Shasha, B. S., Doane, W. M., and Russell, C. R. J. Polym. Sci., Polym. Lett. Ed. (1976) 14(7):417-420.
6. Feldmesser, Julius, Shasha, B. S., and Doane, W. M. Proceedings 1976 Controlled Release Pesticide Symposium, Akron, Ohio, September 13-15, 1976, pp. 6.18-6.29.
7. Schreiber, Marvin. Efficacy and Persistence of Starch Encapsulated EPTC. Presented at the Northcentral Weed Control Conference, Omaha, Nebraska, December 7-9, 1976.

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